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DETERGENT COMPOSITIONS

Field of the Invention

The invention relates to detergent compositions comprising montmorillonite clay.

Background of the Invention

Clays have been added to detergent compositions for a variety of reasons, including for use as a disintegrant in tablets, as mentioned in EP-A-466484. Clay is also used as a fabric softening agent, since it deposits on the surface of fabrics and imparts a soft feel to the fabric. This fabric softening effect is in particular mentioned in US-A-4,062,647.

Although clay in low amounts can give a disintegration effect, high local amounts of clay unfortunately can tend to impede disintegration rather than promote it. This is because there can be a tendency for high local clay contents to gel upon contact with water so as to form a localised gel layer which hinders penetration of water and thus inhibits dispersion of the detergent composition.

It would be desirable to generate a detergent composition, particularly one in tablet form, comprising a clay with less of a tendency to swell and gel on uptake of water from the wash liquor, and thereby improve the dispensing of the composition. An improved fabric softening benefit would also be desirable.

Summary of the Invention

According to one embodiment of the invention a detergent composition is provided, comprising montmorillonite clay, the montmorillonite clay having a crystalline structure which is destroyed after being submitted to acid treatment.

Preferably the composition comprises at least 5% by weight of clay, more preferably at least 8%, and most preferably at least 10% by weight of clay. The composition may be in liquid, gel, powder, granulated form preferably with a bulk density of more than 600 grams per litre, more preferably of more than 700 grams per litre, and most preferably of more than 750 grams per litre, or in tablet form.

Optionally, the tablet may comprise one or more discrete first regions and one or more discrete second regions, and the clay is more highly concentrated in the or each first region than in the or each second region. The concentration of clay in the or each first region may be 2 to 5 times the concentration in the or each second region, when the clay concentration in the or each first region is at least 10% by weight of the or each first region.

Detailed Description of the Invention

The invention relates to a montmorillonite clay. Typically, a montmorillonite clay has a structure which corresponds to the following formula:

$$[\,Si_8\,]\,[\,Al_{4-x}\,Mg_x\,]\,O_{20}\,(OH)_4\;\;R\;^{n}{}_{x/n}$$

R is an exchangeable cation with a valence n (often n=1 or n=2, for example if R is one of Na+, K+, Ca++ or Mg++), this in order to neutralise the cationic exchange capacity x of the clay.

Such clays are widely used in the detergent industry for the fabric softening benefit they provide when washing laundry.

Montmorillonite clays have a crystalline structure. When submitting Mg-saturated / air - dried samples of montmorillonite clays to X-ray diffraction, a 1st order maximum diffraction spacing of ~ 14 to 15 Å is obtained from (00l) planes. This maximum becomes ~ 17 to 18 Å after solvation with glycerol.

The crystalline structure of the montmorillonite clays is more or less resistant to acid treatment. By acid treatment, it is meant to place a sample of clay (e.g. 1g / L) in a 1N HCl solution for 15 hours at a solution temperature of 80°C.

It should be mentioned that most clays can be destroyed by acid treatment, for example after HF treatment. According to the invention, the acid treatment is a HCl acid treatment as described above, and is a specific treatment, and a treatment milder than exposure to HF for example.

Montmorillonite clays [Mg-saturated / air - dried samples] presently used in detergent compositions will still exhibit a maximum diffraction spacing of ~ 14 to 15 Å from (001) planes after such acid treatment when submitted to X-ray diffraction.

It was surprisingly found that it is preferred to use in a detergent composition, an acid - sensitive montmorillonite clay, i.e. a montmorillonite clay which crystalline structure is destroyed after being submitted to said HCl acid treatment. Indeed, use of such a clay has a beneficial effect onto softness and dispersion of the detergent composition in an aqueous medium. Destruction of the crystalline structure is exhibited by the fact that the diffraction spacing of ~ 14 to 15 Å from (001) planes does not appear in the spectrum obtained by X-ray diffraction.

Without wishing to be bound by theory, we believe that this sensitivity towards HCl acids is linked to an increased substitution Mg for Al in the octahedral layer of the montmorillonite clay.

It is preferred that the ratio of Al_2O_3/MgO (% by weight - elemental analysis of the clay) is less than 4 for a montmorillonite clay in order to provide softness and dispersion benefits when using the montmorillonite clay in a detergent composition. More preferably the ratio of Al_2O_3/MgO is less than 3.

The defined clays of the composition of the invention are characterised by a reduction in the tendency to gel, thereby improving the dispensing properties of the composition. These clays have also been found to give improved fabric softening benefits.

For fabric softening purposes the composition may comprise a relatively high clay concentration. Usually, the clay concentration will be at least 5% by weight of the composition. Most frequently the clay content will be at least 8%, preferably at least 10%, by weight of the tablet, but usually less than 25%,

more preferably less than 20%, and most preferably less than 15% by weight of the composition.

When the composition is a tablet, the clay may be substantially uniformly distributed throughout the tablet, in particulate or granular form. Disintegration, and possible softening effects, will therefore be promoted throughout the tablet. Alternatively, the concentration of the clay can be higher in one or more first regions of the tablet than in one or more second regions of the tablet. For example in one embodiment the first regions may contain an amount of clay which is at least 1.5 times, and often 2 to 5 times, the amount of clay in the second regions. By this means it is possible to arrange for the first regions to disperse more rapidly than the second regions. The amount of clay in the first regions is usually at least 5% and often at least 10% by weight of the first regions. The amount of clay in the second regions is usually at least 0.1%, for instance 1 to 5%, by weight of the second regions. Usually at least 60% by weight of the total amount of clay, and often 70 or 75% up to 80 or 90%, by weight of the total amount of clay is in the or each first region with the balance being present in the or each second region.

The tablet will frequently contain at least 5% by weight laundry surfactants, usually including non-ionic and/or anionic surfactants. If desired, the surfactant also may be present in a higher concentration in some regions than other regions (e.g., at least 1.5 times and usually 2 to 5 times). Generally at least 5% by weight non-ionic and/or anionic surfactant is present in any first regions of the tablet, which have a higher clay concentration than remaining regions of the tablet.

Laundry enzyme is often included in the tablet. When the clay is present in a higher concentration in one or more first regions, it is preferred for more enzyme to be in these regions than in the other regions, for instance the amount in the first regions should be normally at least 1.5 times and often at least 2, preferably at least 5 times the amount in the other regions, in order that the enzyme is dispersed as rapidly as possible with the fast dispersing first regions into the wash water.

The tablet often contains laundry bleach. If the clay is more highly concentrated in one or more first regions than second regions, the concentration of bleach is preferably higher in the second regions than the first regions. Preferably the concentration of the bleach in the or each second region is at least 1.5 times the concentration in the or each first region and preferably substantially all the bleach is in the or each second region.

It is generally preferred that the tablet should also contain a flocculant for the clay, in order to aid deposition of the clay on the surface of the fabric. It is usually preferred to include the flocculant in one or more second regions which will disperse more slowly than the first regions. Preferably substantially all the flocculant is in the or each second region.

Typically, the first regions contain 20 to 80%, often around 40 to 60% and usually about 50%, by weight of the tablet with the second regions, or any regions not being the first regions, containing the remainder. The discrete first and second regions may be domains or other zones within the tablet, for example created by forming discrete granules in the tablet, typically having a diameter above 1mm, which have a composition differing from other granules in the tablet, or from the remainder of the tablet.

It is not essential that all the first regions should be of the same composition, or that all second regions should be of the same composition, and there can be one or more first regions having a different composition from the other first regions, and/or one or more second regions having a different composition from the other second regions.

Preferably, each region of the tablet is a layer of the tablet. It is often preferred that there should be three layers, with the tablet typically being a sandwich between similar layers on each outer surface and a different central layer. Different layers may be differently colored.

The tablet is of a size which is convenient for dosing compositions in a washing machine. The preferred size is 10 to 150g, and can be adjusted in accordance with the intended wash load and the design of washing machine to be used.

Tablet Manufacture

Detergent tablets of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

The ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet compressed using a force of less than 2500N.

The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige(r) CB and/or Lodige(r) KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components

of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy(r), Korch(r), Manesty(r), or Bonals(r)). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m2, preferably not exceed 30000 kN/m2, more preferably not exceed 5000 kN/m2, even more preferably not exceed 3000kN/m2 and most preferably not exceed 1000kN/m2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Coating

Solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dispersion.

In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and

shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dispersed under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. The coating material has a melting point preferably of from 40°C to 200°C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40°C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200°C are not practicable to use. Preferably, the materials melt in the range from 60°C to 160°C, more preferably from 70°C to 120°C.

By "melting point" is meant the temperature at which the material when

heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings of the present invention are very hard and provide extra strength to the tablet.

In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dispersion of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, alginic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Tensile Strength

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation :

$$= \frac{2F}{\pi Dt}$$

Where F is the maximum force (Newton) to cause tensile failure

(fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet.

(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

<u>Effervescent</u>

In another preferred embodiment of the present invention the tablets further comprises an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,

i.e. $C_6H_8O_7 + 3NaHCO_3 \quad Na_3C_6H_5O_7 + 3CO_2 + 3H_2O$

Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet

without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dispersion aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dispersion aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et all, ISBN 0-8247-8044-2.

Detersive surfactants

Surfactant are comprised in the tablet according to the invention.

Non-limiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C11-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C20 alkyl sulfates ("AS"), the C10-C18 secondary (2,3) alkyl sulfates of the formula CH3(CH2)x(CHOSO3-M+) CH3 and CH3 (CH2)y(CHOSO3-M+) CH2CH3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C10-C18 alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), C10-C18 alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C10-18 glycerol ethers, the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, and C12-C18 alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 92/06154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C12-C18

glucamides can be used for low sudsing. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts. In a preferred embodiment, the tablet comprises at least 5% per weight of surfactant, more preferably at least 15% per weight, even more preferably at least 25% per weight, and most preferably between 35% and 45% per weight of surfactant.

Non gelling binders

Non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dispersion.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry

addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline

layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSixO_2x+1.yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$Mz(zAlO_2)y].xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in

U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and

substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C12-C18 monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the

various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleach

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January

6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

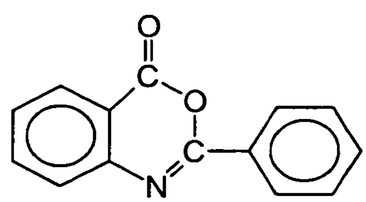
R1N(R5)C(O)R2C(O)L or R1C(O)N(R5)R2C(O)L

wherein R1 is an alkyl group containing from about 6 to about 12 carbon atoms, R2 is an alkylene containing from 1 to about 6 carbon atoms, R5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced

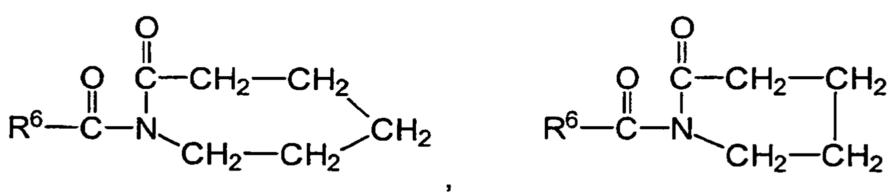
from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by

reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include MnIV2(u-O)3(1,4,7-trimethyl-1,4,7-triazacyclononane)2(PF6)2, MnIII2(u-O)1(u-OAc)2(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO4)2, MnIV4(u-O)6(1,4,7-triazacyclononane)4(ClO4)4, MnIIIMnIV4(u-O)1(u-OAc)2-(1,4,7-trimethyl-1,4,7-triazacyclononane)2(ClO4)3, MnIV(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH3)3(PF6), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Enzymes

Suitable enzymes for use in the compositions of the present invention include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, mannanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. A preferred combination is a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800. Preferred are these cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable

cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.
Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Enzymatic system may be used as bleaching agents : The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.
Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.
Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.
Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent

usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^{R} and Lipomax^{R} (Gist-Brocades) and Lipolase^{R} and Lipolase Ultra^{R}(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.
Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).
The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO

91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from <u>*Bacillus*</u> in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme

corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

More preferred proteases are multiply-substituted protease variants. These protease variants comprise a substitution of an amino acid residue with another naturally occuring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occuring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to

0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk). Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Preferred are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Preferably, the variants are those demonstrating improved thermal stability, more preferably those wherein at least one amino acid residue equivalent to F180, R181, G182, T183, G184, or K185 has been deleted from the parent α-amylase. Particularly preferred are those variants having improved thermal stability which comprise the amino acid deletions R181* + G182* or T183* + G184*. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermal stability and a higher activity level are described in WO95/35382.
The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001 % to 2%, preferably from 0.00018% to

0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described,

for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Flocculants

Most clay flocculating polymers are fairly long chained polymers and co-polymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone and ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acrylamide or acrylic acid. These polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights are in the range of from 100 000 to 10 million. Preferred are such polymers having a weight average molecular weight of from 150000 to 5 million.

The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

Typically, a tablet according to the invention is used in a process to wash and soften laundry in a laundry washing machine.

Examples

SOFTNESS-THROUGH-THE-WASH PERFORMANCE.

Test conditions:

- Miele washing machine at 40 or 60°C cycle and 75g detergent / wash.
- The load consists of 2kg clean cotton fabrics and softness tracers.
- Two sets of softness tracers [¼ of a preconditioned (*) new cotton terry towel] are used;
    1. mono cycle tracers washed once [3 replicates / load and 4 load replicates]
    2. cumulative tracers washed 4X [6 replicates]

(*) *preconditioning of terry towels = new towels, washed 3X at 90°C with granular Ariel Futur [2X] and water [1X]*

- Prior to the grading for softness by expert judges, the softness tracers are line-dried.
- For grading the softness, a 0 -> 4 psu (*) scale [Scheffe] is used where 0 stand for no difference and 4 means a very big difference.

  (*) *psu = panel score units*
- Products tested: Bold 2 in 1

  A] with 13% Quest montmorillonite clay [= reference]

  B] with 13% Quest 5A montmorillonite clay [= invention]

Results [softness grading]

	PSU [benefit vs reference "A"]
Monocycle softness	+ 0.9 s
Cumulative softness	+ 1.2 s

s = statistically significant at 95% confidence level

Examples

Clay Dispersibility

For the purpose of this invention, the dispersibility of the clay is characterised by the rate at which a tablet of clay is dispersed in water. The test is conducted as follows:

40g of clay raw material is introduced in a circular die with a diameter of 54mm and compressed to give a tablet with a diametrical fracture of 5kPa.

The clay tablet is placed in a perforated 10cm diameter metallic cage with a mesh size of 5mmx5mm. The cage is placed in a pool of 5l of demineralised water at 20°C and rotated at a rate of 80rpm. The residue left in the cage after a residence time of 1, 3 or 5 min in the pool of water is determined by weighing. The level of clay dispersibility is calculated as follows:

$$\text{residue number} = \frac{\text{residue weight}}{\text{original tablet weight}} \times 100$$

The lower the residue number the better the clay. Clays suitable for use in the tablets of this invention have a residue number of less than 10 after a residence time of 5 min in water (preferably within 3 min or more preferably within 1 min). For instance one typical hectorite swelling clay (A) gives a residue over 100 at 5 minutes and 1 minute, a selected swelling clay (B) gives a residue of over 100 at 1 minute but zero at 5 minutes, and a preferred clay (C) according to the invention gives a value of zero at each of 1, 3 and 5 minutes.

<u>Example 1</u>

A detergent base powder of composition A (see table 1) was prepared as follows: all the particulate materials of base composition A were mixed together in a mixing drum to form a homogeneous particulate mixture. During this mixing the binder was sprayed on.

When clay was included, the base powder of composition A was mixed in a mixing drum and diluted with montmorillonite clay extrudate formed using the following process. 500g of the clay were mixed with 250g of distilled water. The resulting mix was fed to a Dome extruder with a screw set at a rpm of 80. The resulting mix was then screened using ATSM screen sets. The extrudates made were then dried in a Sherwood Scientific fluid bed dryer set at 90°C for 30 min. The dried extrudates were screened and the oversize (particles larger than 1700mm) and the fines (particles smaller than 150mm) were removed from the mix.

Tablets were then made the following way, 42.8g of the mixture was introduced into a mould of circular shape with a diameter of 5.4cm and compressed to give a tablet tensile strength (or diametrical fracture stress) of 15 kPa.

The level of residue in the dispenser of a washing machine was assessed by means of the <u>"Tablet Dispensing Test"</u>: Two laundry tablets are placed in Baucknecht WA9850 dispenser. The water supply to the washing machine is set to a temperature of 8°C and a hardness of 21 grains per gram,

the dispenser water inlet flowrate is set to 4 l/min and the flowtime at 78 seconds. The level of tablet residues left in the dispenser is checked by switching the washing machine on with the wash cycle set to wash program 4 (whites/colors, short cycle). The residue number is determined as follows:

$$\text{residue number} = \frac{\text{residue weight}}{\text{original tablet weight}} \times 100$$

Table 1: Detergent base powder composition

	Composition A
	(%)
Anionic agglomerates 1	21.45
Anionic agglomerates 2	13.00
Cationic agglomerates	5.45
Layered silicate	10.8
Sodium percarbonate	14.19
Bleach activator agglomerates	5.49
Sodium carbonate	13.64
EDDS/Sulphate particle	0.47
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.73
Soil Release Polymer	0.33
Fluorescer	0.18
Zinc Phthalocyanine sulphonate encapsulate	0.025
Soap powder	1.40
Suds suppressor	1.87
Citric acid	7.10
Protease	0.79
Lipase	0.28
Cellulase	0.22
Amylase	1.08
Binder	
Cationic Polymer	0.42
PEG 4000	0.725
PEG 1000	0.365

Anionic agglomerates 1 consist of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 consist of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Cationic agglomerates consist of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate consists of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates consists of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/sulphate particles consist of 58% ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor consists of 11.5% silicone oil; 59% of zeolite and 29.5% of water.

When the tablets are free of clay, the residue is high. When 2% of clay C extrudate is included, the residue number is significantly reduced. When 5% of clay C is included, the residue number is reduced further and is low. When 5% of clay B is included, the residue number is similar to the value obtained using 2% clay C.